

DEFLUORIDATION STUDIES OF GROUND WATER USING NATURAL ADSORBENT PREPARED FROM MANGO BARK

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ABSTRACT

Groundwater is counted as a renewable resource and is considered as a major source for fulfilling the exponentially increasing water demand across the world. However this source is depleting with increasing anthropogenic activities and addition of fluorides in the water and thus, deterioration of quality and supply of safe drinking water is a major concern throughout the world. The removal behaviors of fluoride ions from ground water by adsorption method using activated carbon were investigated. Water being one of the most essential substances found in abundance from nature bears the risk of high pollution from various sources where it plays a vital role to serve as a major ingredient to the flora and fauna making it to about 75% found on earth's crust. The aim of this research is to develop a cost-effective environment friendly adsorbent for removal of fluoride from ground water which can be applicable to rural areas of many developing countries. This research paper addresses *Mangifera Indica* (mango) bark for the removal of fluoride. The Activated carbon prepared has been characterized by XRD analysis. Batch experiments have been performed to reveal the influence of various parameters on adsorption experiment such as adsorbent dose (0.5- 2 gm), initial fluoride concentration (10-50ppm) and agitation time (30 – 150 min). The optimal value of 2gm adsorbent dose was observed where the adsorbent showed the maximum defluoridation capacity of 90%. The adsorption isotherms, Langmuir and Freundlich were plotted and from the achieved data, it is observed that both Langmuir and Freundlich isotherms are well-fitted. The present study demonstrated that treated *mangifera indica* bark powder could remediate fluoride contaminated water.

KEYWORDS: Fluoride, Adsorption, Adsorbent & Activated Carbon

Received: Dec 02, 2017; **Accepted:** Dec 22, 2017; **Published:** Jan 10, 2018; **Paper Id.:** IJCPTJUN20181

1. INTRODUCTION

Water delivered to any consumer must be free from pathogenic organisms and must comply with the high requirements of modern hygiene according to the World Health Organization (WHO) where in the quality of water depends upon the location of the source and the state of environmental protection in a given area. The level of fluoride in drinking water is a very important physicochemical factor which must be considered when assessing water quality for human consumption because of its range which is restricted for any human body to consume. Thus, in order to ensure compliance with the prescribed limits World Health Organization (WHO) has recommended maximum concentration for fluoride ions in ground water to be 1.5mg/L [IV]. Due to its existence in the form of minerals in rocks, fluoride tends to pollute the ground water naturally and such a condition is exacerbated by an excess of anthropogenic activities time and again. Phosphate rocks also participate in fluoride pollution due to its rampant exposure to people in various forms and in numerous countries such as Asia, Africa, America and Europe. Such cases are observed where contamination range was observed from 1–35 mg/l in ground

water and 0.01 to 3 mg/L for fresh water [XVI].

If found exceeding the permissible limit, fluoride poses serious health impacts on humans and tends to deteriorate the well-being of plants and animals. Several cases of dental fluorosis have been observed where the toll of affected people has gone up as high as around 200 million. Although fluoride ions hold a substantial importance in terms of consumption in human body where consuming fluoride in the range of 0.8 mg/L to 1.0 mg/L is acceptable for dental and bone stability but proves to be harmful if consumed in excess [VII]. Thus, it is essential to aim for the control of fluoride ions from spreading in order to rule out the possibility of related problems.

To avoid such a situation adsorption analysis is considered apt as one of the most precise and economical method for the removal of fluoride ions from ground water and waste water. To achieve efficient reduction activated carbon is used as a medium due to its optimum adsorbing properties but a commercially available activated carbon is a costly affair where its regeneration is also questionable. Advantages offered by this medium include effective control of fluoride contamination by several researchers. Although various other techniques namely, chemical additive methods, Nalgonda technique, electro coagulation, ion-exchange methods were also used for fluoride removal but results were not apt[X].

Natural adsorbents such as Babool bark, Mango, Java plum and Neem tree barks, Camellia sinensis corn cob gooseberry seeds, Guava bark, Khaya senegalensis fruits etc. which are abundantly available, low cost and economic solution to adsorbent are focused by the researchers instead of the costlier options because of the fact that it is been observed that such natural composites have shown strong affinity towards fluoride removal in drinking water. However in some cases, adsorbents have not shown precise results in fluoride reduction thus the need of an economically strong adsorbent remains unfulfilled [XIV,XV].

In the following study, *Mangifera Indica* (Mango) modified Tree Bark (MIB) has been used as a low cost adsorbent to serve as an alternative for commercially activated carbon to process defluoridation of ground water where the objective of the study tends to be removal of undesirable contamination of fluoride ions from groundwater, economically. This can be observed that the selected MIB holds good capacity to process removal of fluoride where there is easy availability which enhances its feasibility in the future for the removal of other metal ions as well.

2. MATERIALS AND METHODS

2.1 Selection of Adsorbents

Several removal methods of fluoride from ground water are in vogue in various parts of the world. But mostly all methods include high operational costs and they require highly skilled and trained workers for operation. Therefore, we have selected environment-friendly low cost adsorbents prepared from Mango Bark.

2.2. Sample Collection

The sample of Mango (*Mangifera Indica*) Bark was collected from HBTU campus located in Kanpur district of Uttar Pradesh, India. Sample was washed with distilled water in order to remove mud, trash etc. for accuracy. After washing the sample, it was sun-dried for 3-4 days approximately. These naturally dried materials were dried in oven at 70° C for 6 hours followed by grinding of sample to form powder. This grinded powder was then sieved through sieve size of 150, 200 and 300 µm.

2.3. Pre-Treatment of Samples

The powdered sample (100gm) was pre-treated with phosphoric acid (85% by weight) in (1:1). Acids are utilized for digestion of powdered samples. Sample was subjected to continuous stirring, manually at $30 \pm 2^\circ\text{C}$ and then kept for 12 hours.

2.4. Washing of Digested Samples

The digested sample was washed with distilled water until a pH of 7 was achieved. After this, the sample was dried in oven at 70°C for 72 hours.

2.5. Carbonization of Samples

After drying of samples, it was kept in muffle furnace in the absence of oxygen to make activated carbon at $450 \pm 20^\circ\text{C}$ for 1 hour. The sample was kept in silica crucible covered with lid in muffle furnace in order to prevent conversion of the same into ash. The Bark activated carbon (BAC) was then collected and kept inside the desiccator for cooling. It keeps the activated carbon moisture-free. Then the prepared activated carbon i.e. BAC was washed again with distilled water to increase its pH till 7 followed by drying in oven at $80 \pm 5^\circ\text{C}$ for 48 hours. The prepared activated carbon was now ready for use in experiments.

2.6. Adsorbate and Experimentation

By dissolving 221 mg of anhydrous sodium fluoride of AR grade in 1000 ml of deionized water, Fluoride Stock Solution was formed in a volumetric flask. The experiments for the same were conducted in batch adsorption analysis for the initial concentration of fluoride ion of 10 mg/L to 50 mg/L in the laboratory. Furthermore, 250 ml capacity plastic bottles were used for test solution volume of 100 ml where in the bottles in use were wrought at a constant rate of 120 rpm mechanically at a temperature of $30 \pm 2^\circ\text{C}$ which is regulated in an orbital shaker incubator. By withdrawing sample at several time intervals was initiated to compute equilibrium time. UV beam Spectrophotometer operated at 570 nm wavelength was used for observing the removal of fluoride.

3. RESULTS AND DISCUSSIONS

3.1. XRD Analysis

X-ray techniques are a family of non-destructive analytical techniques which reveal information about the crystallographic structure, chemical composition, and physical properties of materials and thin films. XRD of treated bark of *Mangifera Indica* before carbonization and after carbonization were performed to predict changes in the crystal structure of the (MIB). From few decades, X-Ray Diffraction (XRD) analysis techniques were the most popular and prominent techniques in the scientist era for the identification of a crystal study and the nature of material. X-ray diffraction spectroscopy (XRD) analyses were carried out with PANalytical X-ray, Philips Analytical. The spectra were analyzed using Origin software. The peaks obtained show the crystalline nature as in figure 2 after carbonization of bark indicating the porosity of activated carbon and if no peaks or minimum peaks are obtained, it resembles amorphous nature as in figure 1 before carbonization of bark.

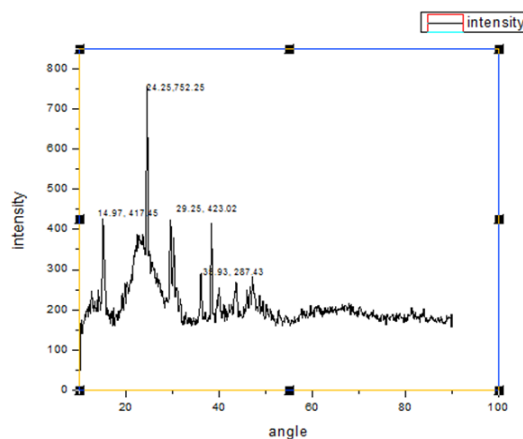


Figure 1: XRD Graph of Bark before Carbonization

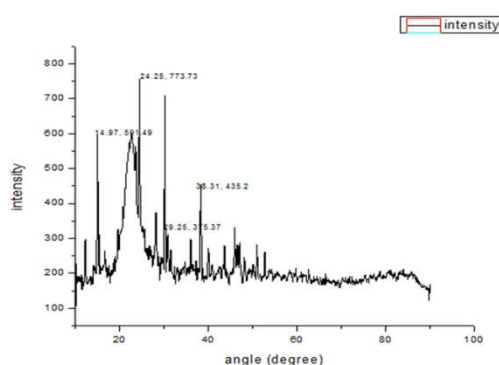


Figure 2: XRD Graph of Bark after Carbonization

3.2. Effect of Contact Time

10-50mg/L of fluoride concentration was taken into the 100 ml beaker and was added with adsorbent dose(0.5g) and were stirred at various time duration ranging from 30, 60, 90, 120 and 150 minutes. All samples once they were removed from the stirrer were filtered using filter paper and the filtrate was analyzed using spectrophotometer.

In figure no. 3, the X-axis represents the time in minute and the Y-axis represent the % removal of fluoride after treatment with the adsorbent. As it can be seen from the figure that when solution was stirred for 30 minutes, % removal for 10mg/L solution is maximum as compared to other solutions. Now as time progresses, % removal also increases. At 60minutes, % removal for 20mg/L solution is 62% but on increasing time from 60 to 90minutes, % removal efficiency is approximately 65%. It is indicated from the figure that the maximum removal is achieved at 90 minutes for all solutions. An amount of 0.5 gm of BAC gives maximum removal efficiency 83% for 10mg/L solution within the time duration of 90 minutes.

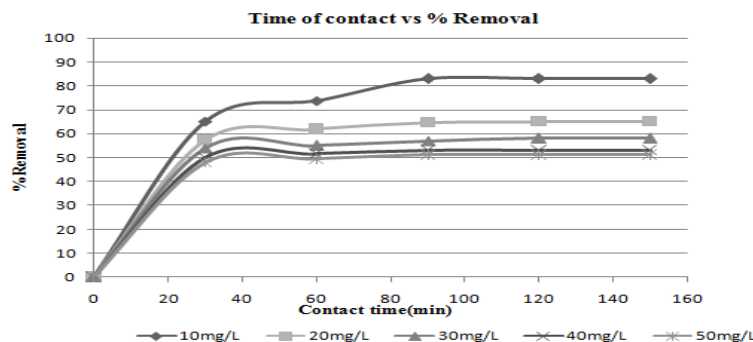


Figure 3: Effect of Contact Time on Fluoride Adsorption at
Adsorbent Dose= 0.5g, Concentration = 10-50mg/L

3.3. Effect of Adsorbent Dosage

Batch adsorption experiment was carried out in stirrer at $30 \pm 2^\circ \text{C}$. Different amounts of BAC (0.5, 1.0, 1.5 and 2.0 gm) was placed into separate beaker of 100ml of 10mg/L to 50mg/L fluoride solution. The mixture in the beaker was subjected to continuous stirring for the time period of 90 minutes. After stirring of 1.5 hours, supernatant was filtered through the filter paper and the filtrate was analyzed using UV-spectrophotometer to find fluoride concentration.

In figure no.4, the X-axis represents the different amount of adsorbent dose in gm and Y-axis represents the % removal of fluoride after treatment with the respective adsorbents. As we can see for 0.5gm of dose (BAC), % removal is 83%, 65%, 58%, 53% & 51% for 10mg/L, 20mg/L, 30mg/L, 40mg/L & 50mg/L solution respectively. On increasing the dose, maximum enhancement in % removal for 10mg/L solution can be observed. It showed the maximum removal by using 2.0 gm of the adsorbent dose. An amount of 2.0 gm of BAC could remove 97.4 % of fluoride from 10mg/L solution.

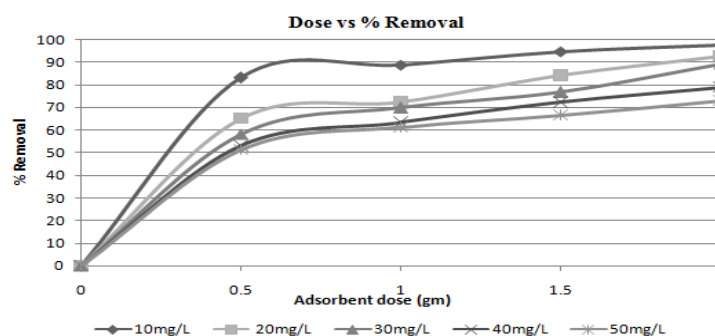


Figure 4: Effect of BAC Adsorbent Dose on Fluoride Adsorption at
Contact Time = 90minutes, Concentration = 10-50mg/L

3.4. Effect of Initial Concentration

Different initial concentrations 10 mg/L, 20mg/L, 30 mg/L, 40 mg/L and 50 mg/L were taken. With increase in the initial fluoride concentration, adsorbent material exhausted slowly shown in figure5. Higher capacity of adsorption found in lower concentrations of fluoride.

In figure no.5, the X-axis represents initial concentration in mg/L and Y-axis represents the % removal of fluoride after adsorption. As we can see when initial concentration is 10mg/L and dosage is 0.5gm, % removal is 83%. On increasing the concentration of fluoride ions from 10mg/L to 20mg/L, 65% removal can be observed. As the concentration increases, % removal efficiency is decreased. It showed that maximum removal is obtained for 10mg/L solution.

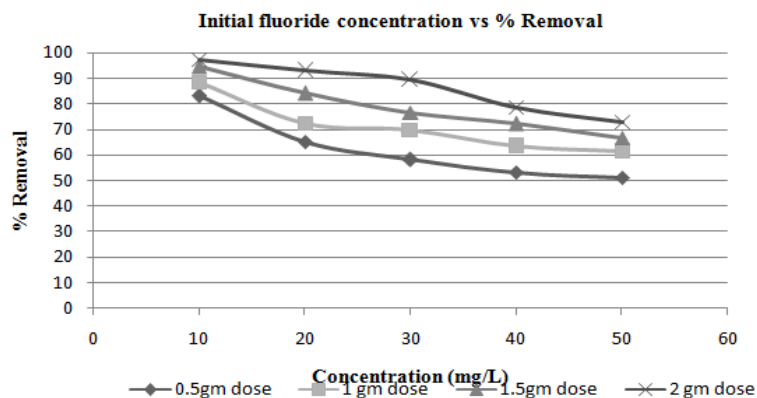


Figure 5: Effect of Initial Fluoride Concentration on Fluoride Adsorption at Contact Time =90minutes, Dosage= 0.5-2.0gm

4. ADSORPTION MODELS

Adsorption isotherms are essential to know how fluoride concentration will interact with prepared carbons and are useful to optimize the use of activated carbon as an adsorbent. It also provides an approximate estimation of the sorption capacity of the adsorbents. Therefore, empirical equations (Freundlich and Langmuir isotherm model) are important for adsorption data interpretations and predictions. Both Freundlich and Langmuir isotherm models are used for the evaluation of experimental results. The Langmuir isotherm is a pre assumption which describes that the removal due to monolayer adsorption takes place on a homogeneous surface of adsorbent without any collaboration between adsorbed particles whereas Freundlich is equilibrium adsorption on the heterogeneous surfaces [II].

Langmuir equation is commonly written as;

$$C_e/q_e = 1/(q_m \cdot K_L) + C_e/q_m \quad (1)$$

In equation (1), the fluoride adsorption capacity is denoted by q_e in mg/g and q_m is the maximum amount adsorbed in mg/g; the equilibrium fluoride concentration is denoted by C_e in mg/L; Constant for Langmuir isotherm is represented by K_L in L/mg.

The linearised Freundlich adsorption isotherm, is of the form

$$\log(q_e) = \log K_f + (1/n) \log C_e \quad (2)$$

In equation (2), the equilibrium fluoride concentration is indicated by C_e and q_e is the amount adsorbed in mg/g; K_f is the empirical constant of Freundlich in mg/g and $1/n$ is the Freundlich exponent. The linear plot shows the Langmuir and Freundlich isotherm application in Figure 6 and 7 respectively.

The data plot showed that equilibrium data fitted well in Freundlich isotherms as well as Langmuir isotherms. But as value of R^2 is more in Freundlich isotherm ($R^2 = 0.99$) as compared to Langmuir isotherm ($R^2 = 0.98$) so it is more favorable to Freundlich isotherm. Figure 6 shows the Langmuir isotherm.

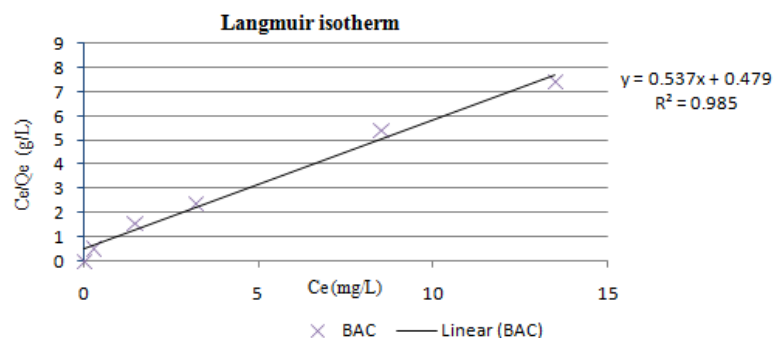


Figure 6: Langmuir Isotherm

Since the data fitted well in Freundlich isotherm so the study predicted that surface of adsorbent is heterogeneous and is suitable for adsorption. Figure 7 shows the Freundlich isotherm.

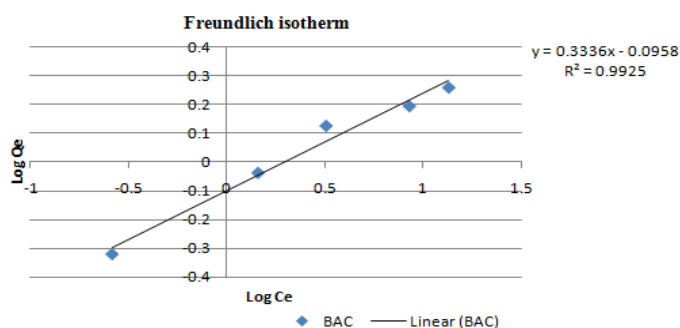


Figure 7: Freundlich Isotherm

5. CONCLUSIONS

Results show that the natural adsorbent prepared from Mango bark which is easily available could be fruitfully used for the fluoride removal over a wide range of concentrations. It has found from the observations and the results that the adsorbent prepared from Mango bark required pre-treatment for the removal of fluoride ions from ground water. On varying time of contact at dose 0.5gm for fluoride concentrations 10mg/L to 50mg/L, the optimum time of contact was found 90 minutes. The treated adsorbent could remove maximum of fluoride concentration at 2.0gm dosage and give maximum removal efficiency for 10ppm fluoride solution. At minimum initial concentrations, maximum removal was recorded. XRD results showed that after carbonization of adsorbent, porosity increased significantly. Adsorption model of (MIB) was well fitted in Freundlich isotherm as well as in Langmuir isotherm.

6. REFERENCES

1. Clifford D, Matson J, (1978), Activated alumina: Rediscovered "adsorbent" for fluoride, humic acids and silica. *Ind. Water Eng.*, 15.
2. Hao O.J., Huang C.P, (1986), Adsorption characteristics of fluoride onto hydrous alumina, *Journal of environmental Engineering*. 112, 1054-1069.
3. Wasay S.A., Tokunaga S, (1996), Removal of hazardous anions from aqueous solutions by La (III) - and Y (III) - impregnated alumina, *Sep.Sci.Technol.*31, 1501-1514.
4. Karthikeyan G., Sundarraj S., (1999), Defluoridation processes, *International Journal of Scientific & Technology Research*.

5. Puri B.K., Balani S., (2000), Trace determination of fluoride using lanthanum hydroxide supported on alumina, *J. Environ. Sci. Health Part A: Toxic/Hazardous Subst. Environ. Eng.* 35, 109-121.
6. Cengeloglu Y., Kir E., Ersoz M., (2002), Removal of fluoride from aqueous solution using red mud, *Separation and purification technology*.
7. Sivabalan R., Rengaraj S., et al., (2003), Cashewnut sheath carbon: A new sorbent for defluoridation of water, *Indian Journal of Chemical Technology*, Vol. 10, Issue 2(217-222).
8. M.A.Q. Rasheed, (2005), New inorganic ion-exchange material for selective removal of fluoride from potable water using ion-selective electrode, *American journal of environmental science*, 1-40.
9. Sharma A., Bhattacharya K.G., (2005), Neem leaf powder as an adsorbent for removal of Cd(II) from aqueous solution, *Journal of hazardous materials*, B 125, 102- 112.
10. Sai Sathish R., Raju N.S.R., et al., (2007), Equilibrium and Kinetic Studies for Fluoride Adsorption from Water on Zirconium Impregnated Coconut Shell Carbon, *Separation Science and Technology*.
11. Vaish A.K., Vaish P., (2009), A Case Study of Fluorosis Mitigation in Durgapur District, Rajasthan, India, 3rd International Workshop on Fluorosis Prevention and Defluoridation of Water.
12. Jaganmohan P., Narayana S.V.L., (2010), Studies on the Evaluation of Angiotensin-I Converting Enzyme Polymorphism under Fluorosis Mediated Renal Failures in Nellore District Andhra Pradesh, India, *Global Journal of Molecular Sciences*, 74-79.
13. Brindha K., Elango L., (2011), Fluoride in Groundwater: Causes, Implications and Mitigation Measures, Applications and Environmental Management, 111-136.
14. Goyal S., Sharma A., (2014), Removal of Fluoride from Drinking Water By Natural Adsorbent, *International Journal of Engineering Research & Technology (IJERT)*.
15. Mridul N., Gupta S.K., (2015), Removal of Chromium (VI) from Aqueous Solution by using Mango, Neem and Eucalyptus Tree Parts, *International Journal of Chemical Sciences and Applications*, Vol 6, Issue 1, pp 37-41.
16. Waghmare S. S., Arfin T., et al., (2015), Preparation and Characterization of *Polyalthia longifolia* Based Alumina as a Novel Adsorbent for Removing Fluoride from Drinking Water, *Asian J. Adv. Basic Sci.* 4(1), 12-24.
17. Abdulaziz Y.I., Esmail A.A., (2016), Adsorption of Pb (II) Ions from Aqueous Phase using Activated Carbon prepared from Novel Precursor, *International Journal of Current Engineering and Technology*.
18. Patil R.N., Nagarnaik P.B., et al., (2016), Removal of fluoride from ground water by using treated bark of *phyllanthus emlica* (amla) tree, *International Journal of Civil Engineering and Technology (IJCET)* 11-20
19. Brito M.J.P., Veloso C.M., et al., (2017), Activated carbons preparation from yellow mombin fruit stones for lipase immobilization, *Fuel Processing Technology* 156, 421-428.
20. Ravulapalli S., Kunta R., (2017), Defluoridation studies using activated carbon derived from the barks of *Ficus racemosa* plant, *Journal of fluorine chemistry*, 193, 58-66.